ON THE THERMAL EXPANSION IN Cu_3Au ALLOY

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ABSTRACT. Following Muto and Takagi's statistical treatment on AB_3 type of binary ordered alloys, an expression for the thermal expansion coefficient γ as a function of long-range order parameter 's' has been obtained. For the alloy Cu_3Au, values of γ and compressibility χ at temperatures 573°K, 623°K and 643°K have been evaluated and compared with the experimental data. The agreement is fairly satisfactory. The discontinuity of the thermal expansion at the transition temperature found experimentally has been also explained.

INTRODUCTION

Order-disorder phenomena in binary alloy systems belong to the class of 'co-operative' phenomena of considerable intrinsic interest. Numerous metal alloy systems have substitutional solid solutions which exhibit superlattice formation near simple stoichiometric concentrations (Nix and Shockley, 1938). The theoretical investigations of the order-disorder transition in substitutional binary alloys mainly deal with the AB type of superlattice due to mathematical simplicity. The theory of the stability of superlattices as a function of temperature, was successfully developed by Bragg and Williams (1934, 35) by introducing the long-range order parameter and a reasonable refinement of Bragg-Williams approximation was made by Kirkwood (1938) in the AB type of superlattice. Following Kirkwood's method of solution, Hovi (1955) first obtained an expression for the thermal expansion coefficient for the AB type of superlattice and explained the discontinuity of expansion at the transition temperature in $\beta-CuZn$. In the same year (1955), Muto and Takagi extended the theoretical treatment for the AB type of superlattice to the AB_3 type in a straight forward way. In the present investigation, an expression for the thermal expansion coefficient (as a function of the long-range order parameter) in AB_3 type of binary alloys has been derived from the free energy expression as obtained by Muto and Takagi and the temperature variation of thermal expansion and also of compressibility in partly ordered alloy Cu_3Au have been explained on its basis.

THEORY

Let us consider an alloy system consisting of two types of atoms A and B with N lattice points of which F_AN are α-sites and F_BN are β-sites (here F_A and F_B denote fractions of A atoms and B atoms respectively). It is assumed that each α-site has z neighbours all β-sites and each β-site has z neighbours, of which $z\, F_A/F_B$ are α-sites and $z\,(F_B-F_A)/F_B$ are β-sites.

In the state of perfect order, all α-sites are occupied by A-atoms and all β-sites by B atoms. In the state of complete disorder, every lattice sites will be occupied on the average by A atoms and B atoms in proportion to their number $F_A : F_B$. In the intermediate order-states, the average distribution can be completely described by the Bragg-Williams order parameter or long-range order 's' defined by :

$$s = \frac{r_\alpha - F_A}{1-F_A} = \frac{r_\beta - F_A}{1-F_B}$$

where $r_{\alpha(\beta)}$ is the fraction of $\alpha(\beta)$ sites occupied by A(B) atoms and 's' is unity for perfect order and zero for the disordered state.

For AB_3 type of superlattices, with $F_A = 1/4$ and $F_B = 3/4$, Muto and Takagi (1955) considering Bragg-Williams approximation obtained the following expression for the 'configurational free energy' from a generalised statistical treatment :

$$F(s)-F(o) = \frac{NKT}{16}\Big[(1+3s)\log(1+3s)+6(1-s)\log(1-s)+(9+3s)\log\left(1+\frac{s}{3}\right)-\frac{zu}{kT}s^2\Big] \quad \ldots \quad (1)$$

where u = ordering energy $= u_{AB}-(u_{AA}+u_{BB})/2$ and $u>0$ for the formation of superlattice structure.

k = Boltzmann constant.

T = Temperature in °K.

Now, minimizing the free energy by the condition :

$$\frac{\partial F}{\partial s} = 0$$

we obtain from the equation (1) :

$$K = \frac{u}{2kT} = \frac{3}{4sz}\log\frac{(1+3s)\left(1+\frac{s}{3}\right)}{(1-s)^2} \quad \ldots \quad (2)$$

which gives equilibrium values of 's' at different temperatures T.

On simplification :

$$K = \frac{4}{z}-\frac{8}{3z}s+\frac{196}{27z}s^2-\frac{400}{27z}s^3+\ldots\ldots \quad \ldots \quad (2a)$$

Differentiating equation (1) with respect to volume v and taking into account that $\dfrac{\partial F}{\partial s} = 0$, we obtain for pressure :

$$p = -\frac{NkTz}{8}\, s^2 \frac{\partial K}{\partial v} \tag{3}$$

where $s = s(v, T)$ and $K = K(v, T)$.

Using thermodynamic relations, it now follows from the above equation (3)

$$\frac{\gamma}{\chi} = \left[\frac{\partial p}{\partial T}\right]_v = -\frac{Nkz}{8}\left[s^2 \frac{\partial K}{\partial v} + T\left\{2s\frac{\partial s}{\partial T}\frac{\partial K}{\partial v} + s^2 \frac{\partial^2 K}{\partial T \partial v}\right\}\right] \qquad \ldots \tag{4}$$

and

$$\frac{1}{\chi} = -v\left[\frac{\partial p}{\partial v}\right]_T = v\,\frac{NkzT}{8}\left[2s\frac{\partial s}{\partial v}\frac{\partial K}{\partial v} + s^2\frac{\partial^2 K}{\partial v^2}\right]$$

where γ = Thermal expansion coefficient, and χ = compressibility. (5)

Hence, the thermal expansion coefficient :

$$\gamma = -\frac{s\dfrac{\partial K}{\partial v} + 2T\dfrac{\partial s}{\partial T}\dfrac{\partial K}{\partial v} + sT\dfrac{\partial^2 K}{\partial T \partial v}}{2vT\dfrac{\partial s}{\partial v}\dfrac{\partial K}{\partial v} + svT\dfrac{\partial^2 K}{\partial v^2}} \tag{6}$$

COMPARISON WITH RESULTS

Let us now apply the theory to the case of face-centred cubic Cu_3Au superlattice for a quantitative comparison between theory and experiment.

(i) *Thermal expansion coefficient at different temperatures*

In order to evaluate the thermal expansion coefficient γ at different temperatures from the expression (6), the derivatives $\dfrac{\partial s}{\partial T}$, $\dfrac{\partial s}{\partial v}$, $\dfrac{\partial K}{\partial v}$, $\dfrac{\partial^2 K}{\partial T \partial v}$ and $\dfrac{\partial^2 K}{\partial v^2}$ are to be obtained.

Since $s = s(v, T)$ and also $K = K(v, T)$, we have the following relations :

$$\left(\frac{\partial s}{\partial T}\right)_p = \left[\frac{\partial s}{\partial T}\right]_v + \left[\frac{\partial s}{\partial v}\right]_T \left[\frac{\partial v}{\partial T}\right]_p$$

or,

$$\left[\frac{\partial s}{\partial v}\right]_T = \left[\frac{\partial T}{\partial v}\right]_p \left[\left[\frac{\partial s}{\partial T}\right]_p - \left[\frac{\partial S}{\partial T}\right]_v\right]$$

and similarly, $\left[\frac{\partial K}{\partial v}\right]_T = \left[\frac{\partial K}{\partial v}\right]_p - \left[\frac{\partial K}{\partial s}\right]_v \left[\frac{\partial s}{\partial T}\right]_v \left[\frac{\partial T}{\partial v}\right]_p$

Hence, using the above relations and the x-ray data reported by Keating and Warren (1951) and Owen and Liu (1947) of long-range order parameters and lattice parameters at different temperatures for the alloy Cu_3Au, we compute the values of $\left[\frac{\partial s}{\partial v}\right]_T$ and $\left[\frac{\partial K}{\partial v}\right]_T$. For the higher derivative $\frac{\partial^2 K}{\partial v^2}$, we have to make the approximation $\frac{\partial}{\partial v}\left[\left[\frac{\partial K}{\partial v}\right]_T\right]_T \simeq -\frac{\partial}{\partial v}\left[\left[\frac{\partial K}{\partial v}\right]_T\right]_p$ (neglecting the higher order terms), since lack of suitable data does not permit us to obtain the exact derivative. The validity of this approximation is tested from the evaluation of the compressibility factor χ from the expression (4) using the theoretically determined values of the expansion coefficient γ. The values of all the parameters of expression (6) are tabulated in Table I while the theoretical and experimental values of the expansion coefficient and compressibility are given in Table II. The experimental values of χ, according to Siegel (1940), do not have high precision. It now appears from the observation of Table II that the present approximation is quite justified and the theory satisfactorily explains the temperature variation of the thermal expansion coefficient for the Cu_3Au superlattice. The temperature variation of compressibility reveals that there is a dependence of χ on order.

TABLE I

Values of the parameters required for the evaluation of γ

T°K	s	$v^{(1)}$ (in Å³)	$\frac{\partial s}{\partial T}$	$\frac{\partial s}{\partial v}$	$\frac{\partial K}{\partial v}$	$\frac{\partial^2 K}{\partial T \partial v}$	$\frac{\partial^2 K}{\partial v^2}$
573	0.765	53.28	−0.001819	0.2063	−0.3910	0.002000	−0.6636
623	0.647	53.46	−0.003353	0.1731	−0.2456	0.003143	−1.0220
643	0.568	53.53	−0.004392	0.1169	−0.1756	0.006255	−1.3160

(1) Owen and Liu (1947)

TABLE II

Theoretical and experimental values of γ and χ at different temperatures

T°K	γ theor. $\times 10^6$ (per °K)	γ expt. $\times 10^6$ (per °K)[1]	χ theor. $\times 10^{11}$ (cm²/dyne)	χ expt. $\times 10^{11}$ (cm²/dyne)[2]
573	68.5	54.1	0.409	0.660
623	86.2	71.8	0.402	0.666
643	118.0	113.5	0.422	0.678

(1) Owen and Liu (1947)
(2) Siegel (1940)

(ii) *Thermal expansion coefficient at the 'Transition-temperature'*

Since $K = K(s)$ as seen from the equation (2), the expression (6) for the thermal expansion coefficient can also be written in the alternative form :

$$\frac{s\dfrac{\partial K}{\partial s}\dfrac{\partial s}{\partial v}+T\left[2\dfrac{\partial s}{\partial T}\dfrac{\partial K}{\partial s}\dfrac{\partial s}{\partial v}+s\left[\dfrac{\partial^2 K}{\partial s^2}\dfrac{\partial s}{\partial v}\dfrac{\partial s}{\partial T}+\dfrac{\partial K}{\partial s}\dfrac{\partial^2 s}{\partial v\partial T}\right]\right]}{vT\left[2\left[\dfrac{\partial s}{\partial v}\right]^2\dfrac{\partial K}{\partial s}+s\left\{\dfrac{\partial^2 K}{\partial s^2}\left[\dfrac{\partial s}{\partial v}\right]^2+\dfrac{\partial K}{\partial s}\dfrac{\partial^2 s}{\partial v^2}\right\}\right]} \quad \ldots \quad (6a)$$

Let us examine this case at the 'Transition Temperature'. Now, as the transition temperature is approached from lower temperatures ($s \rightarrow 0$, $T \rightarrow T_{c-0}$), it follows from (2a) :

$$\lim_{s\to 0}\frac{\partial K}{\partial s} \neq 0 \quad \text{and} \quad \lim_{s\to 0}\frac{\partial^2 K}{\partial s^2}$$

Again, from the nature of the theoretical curve as predicted by Muto and Takagi (1955)and from the x-ray measurements of long-range order on Cu_3Au (Keating and Warren), we find that :

$$\lim_{s\to 0}\frac{\partial s}{\partial T} = \infty$$

Also, from the experimental observations of Owen and Liu (1947), we may write :

$\lim\limits_{s\to 0}\dfrac{\partial s}{\partial v}$ = finite, as it appears that volume is not discontinuous at T_c.

With the assumption that the higher derivatives $\dfrac{\partial^2 s}{\partial v^2}$ and $\dfrac{\partial^2 s}{\partial v\partial T}$ remain finite when $s \rightarrow 0$, we obtain from the above expression (6a), considering all the conditions :

$\lim\limits_{s\to 0}\gamma$ is not finite which suggests that the thermal expansion coefficient is discontinuous at the 'Transition Temperature'.

Now, from the dilatometric observations of Nix and MacNair (1941) on Cu_3Au, we find that the thermal expansion coefficient shows a sharp peak at the transition temperature. It is also found from x-ray measurements of Owen and Liu (1947) that the rate of expansion increases as the transition temperature is approached and the value of the coefficient immediately after the transformation is about half its value immediately before the transformation.

Thus, we may conclude that the theory based on Bragg-Williams approximation is in fair agreement with the experimental observations. But the theory suffers from the limitation that it is not possible to derive the values of expansion coefficient γ in the low temperature region where the order-parameter 's' is almost

$$\left.\begin{aligned}
G &= -\cot 2\phi = \frac{K_1-K_2}{2L} = \frac{\omega_x^2}{2\omega_z(r-\beta')} \\
K_1 &= 1-\frac{\beta'^2-r\beta'-\omega_x^2}{c'}\,r,\ K_2 = 1-\frac{r(\beta'^2-r\beta')}{c'},\ L = \frac{r(r-\beta')\omega_z}{c'} \\
c' &= \beta'(\beta'^2-\omega^2)-r(\beta'^2-\omega_z^2),\ \ \omega_x = \omega\sin\theta,\ \ \omega_z = \omega\cos\theta \\
\beta' &= 1-j\frac{\nu}{p},\ \omega = \frac{p_H}{p},\ p_H = \frac{eH}{mc},\ r = \frac{p_6^2}{p^2} = \frac{4\pi Ne^2}{mp^2} \\
\dot{V} &= \frac{dV}{du},\ \dot{W} = \frac{dW}{du},\ \dot{\phi} = \frac{d\rho/du}{1+\rho^2}
\end{aligned}\right\} \quad \ldots \quad (7)$$

COMPLEX REFRACTIVE INDEX

The well-known Appleton-Hartree formula (1927, 1929) for the square of complex refractive index q is given by

$$q^2 = 1+\frac{1}{(\alpha+j\beta)-\dfrac{\gamma_T^2}{2(1+\alpha+j\beta)}\pm\sqrt{\dfrac{\gamma_T^4}{4(1+\alpha+j\beta)^2}+\gamma_L^2}} \quad \ldots \quad (8)$$

The upper positive sign before the radical in eq. (8) refers to the extraordinary mode and the lower negative sign to the ordinary mode.

The notations in (8) are :

$$\alpha = -p^2/p_6^2,\ p_0^2 = 4\pi Ne^2/m,\ \beta = p\nu/p_0^2$$

$$\gamma = pp_H/p_0^2,\ p_H = eH/mc,\ \gamma_L = \gamma\cos\theta,\ \gamma_T = \gamma\sin\theta$$

where

ν = electron collisional frequency

H = intensity of the earth's magnetic field

e, m = charge and mass of an electron

c = velocity of light in vacuum,

p = angular frequency of the wave,

N = electron number density

and θ = angle between the direction of propagation of the radio-wave and the positive direction of the earth's magnetic field.

In terms of the U.R.S.I. notations, Eq. (8) corresponds to :

$$q^2 = 1-\frac{X}{1-jZ-\dfrac{Y_T^2}{2(1-X-jZ)}\pm\sqrt{\left[\dfrac{Y_T^4}{4(1-X-jZ)^2}+Y_L^2\right]}} \quad \ldots \quad (8.1)$$

The notations in Eq. (8.1) are :

$$X = \frac{4\pi Ne^2}{m\omega^2}\,,\; Y_{L,T} = \frac{eH_{L,T}}{\omega mc}\,,\; Z = \frac{\nu}{\omega}$$

The angular frequency ω of radio-wave is the same as p in the old notation. Associating the *plus* sign before the radical in Eq. (8.1) with the ordinary mode and the *minus* sign with the *extraordinary* mode (Ratcliffe, 1962), it can be easily shown that the minus sign before the radical in Eq. (8) corresponds to the ordinary mode and the plus sign to the extraordinary mode, so that, following the old notations we get for the 0-mode :

$$q_0^2 = 1 + \frac{1}{\alpha + j\beta - \dfrac{\gamma_T^2}{2(1+\alpha+j\beta)} - \sqrt{\left[\dfrac{\gamma_T^4}{4(1+\alpha+j\beta)^2} + \gamma_L^2\right]}} \quad \ldots \quad (8.2)$$

and for the X-mode :

$$q_x^2 = 1 + \frac{1}{\alpha + j\beta - \dfrac{\gamma_T^2}{2(1+\alpha+j\beta)} + \sqrt{\left[\dfrac{\gamma_T^4}{4(1+\alpha+j\beta)^2} + \gamma_L^2\right]}} \quad \ldots \quad (8.3)$$

We next compare these two formulae (8.2), (8.3) with equations (4) and (5) deduced from the coupled wave-equations of Saha, Banerjea and Guha (1951). From (7) it can be easily shown :

$$G = \frac{\gamma_T^2}{2\gamma_L(1+\alpha+j\beta)} \quad \ldots \quad (7.1)$$

Since $\qquad \omega_z = \dfrac{p_H}{p}\cos\theta,\;$ we get :

$$\rho_1\omega_z = (G - \sqrt{1+G^2})\,\frac{p_H}{p}\cos\theta$$

$$= \frac{p_0^2}{p^2}\left[\frac{\gamma_T^2}{2(1+\alpha+j\beta)} - \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2} + \gamma_L^2}\right]$$

Hence putting the value of $\rho_1\omega_z$ in Eq. (4), we have

$$q_0^{\,2} = 1 + \frac{1}{\alpha + j\beta - \dfrac{\gamma_T^2}{2(1+\alpha+j\beta)} + \sqrt{\dfrac{\gamma_T}{4(1+\alpha+j\beta)^2} + \gamma_L}}$$

It is seen that the last expression for the square of complex refractive index agrees with Eq. (8.3). Similarly, it can be shown that Eq. (5) agrees with (8.2). Hence Eqs. (4) and (5) should be interchanged as follows :

$$q_x^2 = 1 - \frac{r}{\beta' + \rho_1 \omega_z}$$

and

$$q_0^2 = 1 - \frac{r}{\beta' + \rho_2 \omega_z}$$

COUPLED WAVE-EQUATIONS AND PROPAGATION VECTORS

Saha *et al* (1951) deduced the coupled wave-equations (1) and (1.1) by starting from the following equations :

$$\frac{d^2 E_x}{du^2} + K_1 E_x - jLE_y = 0 \qquad \ldots \quad (9)$$

$$\frac{d^2 E_y}{du^2} + K_2 E_y + jLE_x = 0 \qquad \ldots \quad (9.1)$$

and putting :

$$\begin{pmatrix} E_x \\ jE_y \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} V \\ W \end{pmatrix} \qquad \ldots \quad (10)$$

Using Eqs. (9), (9.1) and (10), it can be easily shown :

$$V'' + [K_1 \cos^2\phi + K_2 \sin^2\phi - 2L \sin\phi \cos\phi) V$$

$$-[(K_1 - K_2) \sin\phi \cos\phi + L(\cos^2\phi - \sin^2\phi)] W = 0 \qquad \ldots \quad (1.2)$$

$$W'' + [K_1 \sin^2\phi + K_2 \cos^2\phi + 2L \cos\phi \sin\phi] W$$

$$-[(K_1 - K_2) \sin\phi \cos\phi + L(\cos^2\phi - \sin^2\phi)] V = 0 \qquad \ldots \quad (1.3)$$

where

$$V'' = \ddot{V} - 2\dot{\phi}\dot{W} - \ddot{\phi} W - \dot{\phi}^2 V \qquad \ldots \quad (11)$$

$$W'' = \ddot{W} + 2\dot{\phi}\dot{V} + \ddot{\phi} V - \dot{\phi}^2 W \qquad \ldots \quad (11.1)$$

The coefficients of the cross-terms in Eqs. (1.2) and (1.3) may be made to disappear by writing $\tan\phi = G \pm 1 + G^2$ as shown by Saha *et al.* Hence there are two values of $\tan\phi$ given by $G + \sqrt{1+G^2}$ and $G - \sqrt{1+G^2}$.

Let us write :

$$\tan \phi_1 = G-\sqrt{1+G^2} = \rho_1 \qquad \dots \quad (12)$$

$$\tan \phi_2 = G+\sqrt{1+G^2} = \rho_2 \qquad \dots \quad (12.1)$$

We next rotate the co-ordinate system through a complex angle $\phi_1 = \tan^{-1}\rho_1$. The equations (1.2) and (1.3) are then reduced to

$$V''_1+[K_1 \cos^2 \phi_1+K_2 \sin^2 \phi_1-2L \sin \phi_1 \cos \phi_1]V_1 = 0 \qquad \dots \quad (1.4)$$

$$W''_1+[K_1 \sin^2 \phi_1+K_2 \cos^2 \phi_1+2L \sin \phi \cos \phi_1]\, W_1 = 0 \qquad \dots \quad (1.5)$$

where

$$V_1'' = \ddot{V}_1-2\dot{\phi}_1\dot{W}_1-\ddot{\phi}_1 W_1 \quad \dot{\phi}_1^2 V_1 \qquad \dots \quad (11.2)$$

$$W''_1 = \ddot{W}_1+2\dot{\phi}_1\dot{V}_1+\ddot{\phi}_1 V_1--\dot{\phi}^2 W_1 \qquad \dots \quad (11.3)$$

$$V_1 = E_x \cos \phi_1+jE_y \sin \phi_1 \qquad \dots \quad (2.1)$$

$$W_1 = -E_x \sin \phi_1+jE_y \cos \phi_1 \qquad \dots \quad (3.1)$$

If we rotate the co-ordinate system through a complex angle $\phi_2 = \tan^{-1}\rho_2$ then the equations (1.2) and (1.3) are reduced to

$$V''_2+[K_1 \cos^2 \phi_2+K_2 \sin^2 \phi_2-2L \sin \phi_2 \cos \phi_2]V_2 = 0 \qquad \dots \quad (1.6)$$

$$W''_2+[K_1 \sin^2 \phi_2+K_2 \cos^2 \phi_2+2L \sin \phi_2 \cos \phi_2]W_2 = 0 \qquad \dots \quad (1.7)$$

where

$$V''_2 = \ddot{V}_2-2\dot{\phi}_2\dot{W}_2-\ddot{\phi}_2 W_2-\dot{\phi}_2^2 V_2 \qquad (11.4)$$

$$W''_2 = \ddot{W}_2+2\dot{\phi}_2\dot{V}_2+\ddot{\phi}_2 V_2-\dot{\phi}_2^2 W_2 \qquad \dots \quad (11.5)$$

$$V_2 = E_x \cos \phi_2+jE_y \sin \phi_2 \qquad \dots \quad (2.2)$$

$$W_2 = -E_x \sin \phi_2+jE_y \cos \phi_2 \qquad \dots \quad (3.2)$$

It is shown in the Appendix that the following relations hold good :

$$K_1 \cos^2 \phi_1+K_2 \sin^2 \phi_1-2L \sin \phi_1 \cos \phi_1 = 1-\frac{r}{\beta'+\rho_1\omega_z} = q_x^2 \qquad \dots \quad (4.1)$$

$$K_1 \cos^2 \phi_2+K_2 \sin^2 \phi_2-2L \sin \phi_2 \cos \phi_2 = 1-\frac{r}{\beta'+\rho_2\omega_z} = q_0^3 \qquad \dots \quad (5.1)$$

$$K_1 \sin^2 \phi_1+K_2 \cos^2 \phi_1+2L \sin \phi_1 \cos \phi_1 = 1-\frac{r}{\beta'+\rho_2\omega_z} = q_0^2 \qquad \dots \quad (5.2)$$

$$K_1 \sin^2\phi_2 + K_2 \cos^2\phi_2 + 2L \sin\phi_2 \cos\phi_2 = 1 - \frac{r}{\beta' + \rho_1\omega_z} = q_x^2 \qquad \ldots \quad (4.2)$$

Hence equations (1.4) and (1.5) should be called the coupled wave-equations for the X-and 0-modes respectively and can be written as :

$$\ddot{V}_1 + (q_x^2 - \dot{\phi}_1^2)V_1 = 2\dot{\phi}_1 \dot{W}_1 + \ddot{\phi}_1 W_1 \text{ (for the } X\text{-mode)} \qquad \ldots \quad (1.8)$$

$$\ddot{W}_1 + (q_0^2 - \dot{\phi}_2^2)W_1 = -2\dot{\phi}_1 \dot{V}_1 - \ddot{\phi}_1 V_1 \text{ (for the 0-mode)} \qquad \ldots \quad (1.9)$$

where,

$$V_1 = \frac{E_x + j\rho_1 E_y}{\sqrt{1+\rho_1^2}} \text{ (for the } X\text{-mode)} \qquad \ldots \quad (2.3)$$

$$W_1 = \frac{-\rho_1 E_x + jE_y}{\sqrt{1+\rho_1^2}} \text{ (for the 0- mode)} \qquad \ldots \quad (3.3)$$

Similarly Eqs. (1.6) and (1.7) can be rewritten as :

$$\ddot{V}_2 + (q_0^2 - \dot{\phi}_2^2)V_2 = 2\dot{\phi}_2 \dot{W}_2 + \ddot{\phi}_2 W_2 \text{ (for the 0-mode)} \qquad \ldots \quad (1.10)$$

$$\ddot{W}_2 + (q_x^2 - \dot{\phi}_2^2)W_2 = -2\dot{\phi}_2 \dot{V}_2 - \ddot{\phi}_2 V_2 \text{ (for the } X\text{-mode)} \qquad \ldots \quad (1.11)$$

where

$$V_2 = \frac{E_x + j\rho_2 E_y}{\sqrt{1+\rho_2^2}} \text{ (for the 0-mode)} \qquad \ldots \quad (2.4)$$

$$W_2 = \frac{-\rho_2 E_x + jE_y}{\sqrt{1+\rho_2^2}} \text{ (for the } X\text{-mode)} \qquad \ldots \quad (3.4)$$

It has been shown in the Appendix

$$W_1 = V_2,\ W_2 = -V_1 \quad \dot{\phi}_1 = \dot{\phi}_2 = \dot{\phi}\text{(say)} \qquad \ldots \quad (13)$$

Hence, using (13), the equations (1.8) (1.9), (1.10) and (1.11) can be combined into two coupled epuations : –

$$\ddot{V}_x + (q_x^2 - \dot{\phi}^2)V_x = 2\dot{\phi}\dot{V}_0 + \ddot{\phi}V_0 \text{ (for the } X\text{-mode)} \qquad \ldots \quad (1.12)$$

$$\ddot{V}_0 + (q_0^2 - \dot{\phi}^2)V_0 = -2\dot{\phi}\dot{V}_x - \ddot{\phi}V_x \text{ (for the 0-mode)} \qquad \ldots \quad (1.13)$$

where,

$$V_x = V_1 = -W_2 = \frac{E_x^{(x)} + j\rho_1 E_y^{(x)}}{\sqrt{1+\rho_1^2}} = \text{Propagation vector for the } X\text{-mode} \qquad (2.5)$$

$$V_0 = V_2 = W_1 = \frac{E_x^{(0)} + j\rho_2 E_y^{(0)}}{\sqrt{1+\rho_2^2}} = \text{Propagation vector for the 0-mode} \quad \ldots \quad (3.5)$$

$$\dot{\phi}_1 = \frac{d\rho_1/du}{1+\rho_1^2} = \frac{d\rho_2/du}{1+\rho_2^2} = \dot{\phi}_2 = \dot{\phi}$$

$$q_x^2 = 1 - \frac{r}{\beta' + \rho_1 \omega_z}, \quad q_0^2 = 1 - \frac{r}{\beta' + \rho_2 \omega_z}$$

Thus it is evident that the equations (1) and (1.1) were *incorrectly* labelled as the coupled wave-equations for the 0-mode and the X-mode respectively. It is shown in the next section that the equations (1) and (1.1) lose all their significance, if they are called the coupled wave-equations for the 0- and X-modes respectively.

WAVE-POLARIZATION

We start from the relations :

$$\begin{aligned} D_x &= q^2 E_x \\ D_y &= q^2 E_y \end{aligned} \quad \ldots \quad (14)$$

The following expressions for the displacement vector were deduced by Saha *et al* (1951).

$$\begin{aligned} D_x &= K_1 E_x - jL E_y \\ D_y &= K_2 E_y + jL E_x \end{aligned} \quad \ldots \quad (15)$$

From (14) and (15)

$$\frac{E_x}{E_y} = \frac{K_2 - q^2 - jL}{q^2 - K_1 - jL} = \frac{q^2 - jL - K_2}{q^2 - K_1 + jL} \quad \ldots \quad (16)$$

Hence from (16)

$$q^2 = \frac{(K_1+K_2) \pm \sqrt{(K_1+K_2)^2 - 4(K_1K_2 - L^2)}}{2} \quad \ldots \quad (17)$$

From (16) and (17)

$$\frac{E_y - E_x}{E_y + E_x} = \pm \frac{\sqrt{(K_2-K_1)^2 + 4L^2}}{(K_2-K_1) - 2jL} \quad \ldots \quad (16.1)$$

Taking the positive sign of Ea. (16.1)

$$\frac{E_y - E_x}{E_y + E_x} = \sqrt{\frac{(K_2-K_1)+2jL}{(K_2-K_1)-2jL}} \quad \ldots \quad (16.2)$$

Since $G = (K_1 - K_2)/2L$ we get :

$$\frac{E_y - E_x}{E_y + E_x} = \sqrt{\frac{G-j}{G+j}} \qquad \ldots \quad (16.3)$$

Putting $G = A\cos\psi$, $1 = A\sin\psi$ where $A = \sqrt{1+G^2}$ we get from (16.3)

$$\frac{E_x}{E_y} = \tanh j\psi/2 \qquad \ldots \quad (16.4)$$

Since $\tan\psi = \frac{1}{G} = -\tan 2\phi$, we have

$$\frac{E_x}{E_y} = -j\tan\phi = -j\rho \qquad \ldots \quad (16.5)$$

The same Eq. (16.5) can be deduced by using the negative sign of Eq.(16.1).

There are two different values of ρ, viz. $\rho_1 = G - \sqrt{1+G^2}$ and $\rho_2 = G + \sqrt{1+G^2}$ and we have

$$\frac{E_x}{E_y} = -j\rho_1 \qquad \ldots \quad (16.6)$$

$$\frac{E_x}{E_y} = -j\rho_2 \qquad \ldots \quad (16.7)$$

Let us now compare these equations (16.6) and (16.7) with the well-known Appleton-Hartree formula (1927-29) for the wave polarization in order to associate eqs. (16.6) and (16.7) with the so-called *O*- and *X*- modes.

Using the right-handed co-ordinate system (Fig. 1) the Appleton-Hartree formula for the wave-polarization in terms of magnetic vector components can be written as :

$$\frac{H_z}{H_y} = \frac{j}{\gamma_L}\left[-\frac{\gamma_T^2}{2(1+\alpha+j\beta)} \pm \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2} + \gamma_L^2}\right] \qquad \ldots \quad (18)$$

where the direction of propagation of the radio wave is along the *X*-axis. In Eqs. (18), (16.6) and (16.7) the sign of the charge has not been taken into consideration.

In deriving the equations (16.6) and (16.7) the co-ordinate system of Fig. 2 has been used. When eq. (18) is referred to the co-ordinate system of Fig. 2, we have :

$$\frac{H_x}{H_y} = -\frac{j}{\gamma_L}\left[-\frac{\gamma_T^2}{2(1+\alpha+j\beta)} + \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2} + \gamma_L^2}\right] \qquad \ldots \quad (18.1)$$

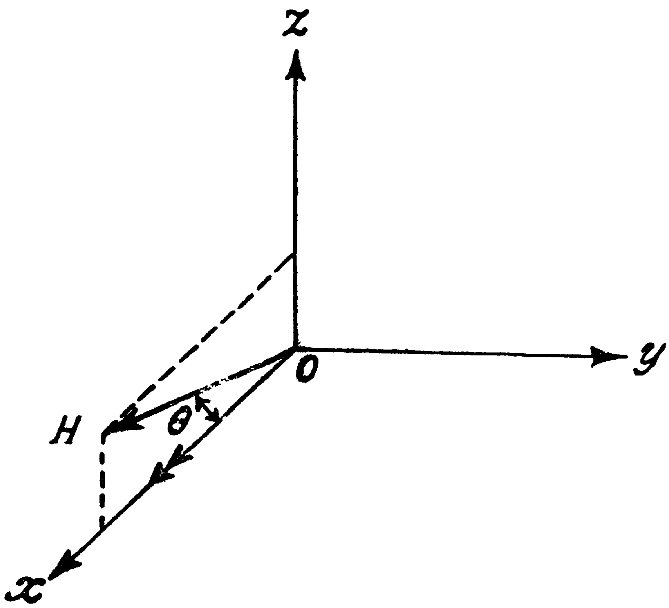

Fig. 1. Co-ordinate system (Saha *et al*).
OH → direction of the earth's magnetic field.
OZ → direction of the radio wave propagation.

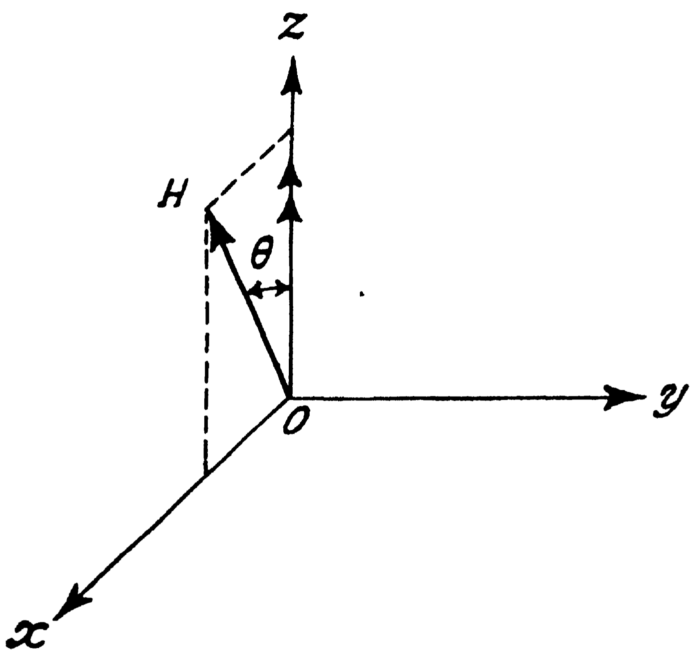

Fig. 2. Co-ordinate system (Appleton)
OH → direction of the earth's magnetic field.
OX → direction of the radio wave propagation.

where the direction of propagation of radio-wave is along Z-axis. Hence for the 0-mode :

$$\left(\frac{H_x}{H_y}\right)_0 = -\frac{j}{\gamma_L}\left[-\frac{\gamma_T^2}{2(1+\alpha+j\beta)} - \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2}+\gamma_L^2}\right] \quad \ldots \quad (18.2)$$

and for the X-mode :

$$\left(\frac{H_x}{H_y}\right)_x = -\frac{j}{\gamma_L}\left[-\frac{\gamma_T^2}{2(1+\alpha+j\beta)} + \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2}+\gamma_L^2}\right] \quad \ldots \quad (18.3)$$

Since $E_x/E_y = -H_y/H_x$ we get from (18.2) and (18.3)

$$\left(\frac{E_x}{E_y}\right)_0 = -\frac{j}{\gamma_L}\left[\frac{\gamma_T^2}{2(1+\alpha+j\beta)} - \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2}+\gamma_L^2}\right] \quad \ldots \quad (18.4)$$

$$\left(\frac{E_x}{E_y}\right)_x = -\frac{j}{\gamma_L}\left[\frac{\gamma_T^2}{2(1+\alpha+j\beta)} + \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2}+\gamma_L^2}\right] \quad \ldots \quad (18.5)$$

From (7.1) and (12)

$$-j\rho_1 = -\frac{j}{\gamma_L}\left[\frac{\gamma_T^2}{2(1+\alpha+j\beta)} - \sqrt{\frac{\gamma_T^4}{4(1+\alpha+j\beta)^2}+\gamma_L^2}\right]$$

Since the above expression for $-j\rho_1$ agrees with (18.4) we have for the 0-mode :

$$\left(\frac{E_x}{E_y}\right)_0 = -j\rho_1 \quad \ldots \quad (16.8)$$

Similarly for the X-node :

$$\left(\frac{E_x}{E_y}\right)_x = -j\rho_2 \quad \ldots \quad (16.9)$$

In view of Eqs. (16.8) and (16.9) it is seen from (2) and (3) that V and W are reduced to zero; hence the equations (1) and (1.1) lose all their significance, if these wave equations (1) and (1.1) are associated with the 0- and X-mode respectively.

RELATION BETWEEN THE ELECTRIC AND MAGNETIC FIELDS

We start from the eqs. of propagation of the magnetic vector (1947) :

$$\frac{d^2H_x}{du^2} + K_2H_x - jLH_y = 0$$

$$\frac{d^2H_y}{du^2} + K_1H_y + jLH_x = 0 \quad \ldots \quad (19)$$

and rotate the co-ordinate system (Fig. 2) through a complex angie ϕ' and put

$$\begin{pmatrix} jH_y \\ H_x \end{pmatrix} = \begin{pmatrix} \cos\phi' & -\sin\phi' \\ \sin\phi' & \cos\phi' \end{pmatrix} \begin{pmatrix} V_H \\ W_H \end{pmatrix} \quad \ldots \quad (20)$$

Using (19) and (20) it can be easily shown :

$$\ddot{V}_H+[K_1\cos^2\phi'+K_2\sin^2\phi'-2L\sin\phi'\cos\phi'-\dot{\phi}'^2]V_H$$

$$-[L(\cos^2\phi'-\sin^2\phi')+(K_1-K_2)\sin\phi'\cos\phi']W_H = 2\dot{\phi}'\dot{W}_H+\ddot{\phi}'W_H \quad \ldots \quad (19.1)$$

and

$$\ddot{W}_H+[K_1\sin^2\phi'+K_2\cos^2\phi'+2L\sin\phi'\cos\phi'-\dot{\phi}'^2]W_H$$

$$-[(K_1-K_2)\cos\phi'\sin\phi'+L(\cos^2\phi'-\sin^2\phi')]V_H = -2\dot{\phi}'\dot{V}_H-\ddot{\phi}'V_H \quad \ldots \quad (19.2)$$

Putting $\dfrac{K_1-K_2}{2L} = G = -\cot 2\phi'$ Eqs. (19.1) and (19.2) are reduced to

$$\ddot{V}_H+[K_1\cos^2\phi'+K_2\sin^2\phi'-2L\sin\phi'\cos\phi'-\dot{\phi}'^2]V_H$$

$$= 2\dot{\phi}'\dot{W}_H+\ddot{\phi}'W_H \quad \ldots \quad (19.3)$$

and,

$$\ddot{W}_H+[K_1\sin^2\phi'+K_2\cos^2\phi'+2L\sin\phi'\cos\phi'-\dot{\phi}'^2]W_H$$

$$=-2\dot{\phi}'\dot{V}_H-\ddot{\phi}'W_H \quad \ldots \quad (19.4)$$

where,

$$V_H = jH_y\cos\phi'+H_x\sin\phi' \quad \ldots \quad (2.6)$$

$$W_H = -jH_y\sin\phi'+H_x\cos\phi' \quad \ldots \quad (3.6)$$

Putting $\dfrac{K_1-K_2}{2L} = G = -\cot 2\phi$ Eqs (1.2) and (1.3) can be written as :

$$\ddot{V}+[K_1\cos^2\phi+K_2\sin^2\phi-2L\sin\phi\cos\phi-\dot{\phi}^2]V = 2\dot{\phi}\dot{W}+\ddot{\phi}W \quad \ldots \quad (1.12)$$

and

$$\ddot{W}+[K_1\sin^2\phi+K_2\cos^2\phi+2L\sin\phi\cos\phi-\dot{\phi}^2]W=-2\dot{\phi}\dot{V}-\ddot{\phi}V \quad \ldots \quad (1.13)$$

Since $\phi = \phi'$, we get from (1.12), (1.13) and (19.3), (19.4)

$$V = V_H \quad \text{and} \quad W = W_H$$

i.e.

$$E_x \cos\phi + jH_y \sin\phi = jH_y \cos\phi + H_x \sin\phi$$

$$-E_x \sin\phi + jE_y \cos\phi = -jH_y \sin\phi + H_x \cos\phi \quad \dots \quad (21)$$

From (21)

$$\frac{H_x}{H_y} = -\frac{E_y}{E_x}$$

APPENDIX

$$\tan\phi_1 = \rho_1 = G - \sqrt{1+G^2} \quad \dots \quad \text{(i)}$$

$$\dots \quad \cos 2\phi_1 = -\frac{\rho_1^2 - 1}{\rho_1^2 + 1} = \frac{G}{\sqrt{1+G^2}} \quad \dots \quad \text{(ii)}$$

$$\tan\phi_2 = \rho_2 = G + \sqrt{1+G^2} \quad \dots \quad \text{(iii)}$$

$$\cos 2\phi_2 = -\frac{\rho_2^2 - 1}{\rho_2^2 + 1} = -\frac{G}{\sqrt{1+G^2}} \quad \dots \quad \text{(iv)}$$

Now,

$$q^2 = K_1 \cos^2\phi_2 + K_2 \sin^2\phi_2 - 2L \sin\phi_2 \cos\phi_2$$

$$= \frac{K_1 + K_2}{2} + \frac{1}{2}(K_1 - K_2)\cos 2\phi_2 - L \sin 2\phi_2$$

Since, $(K_1 - K_2)/2L = G = -\cot 2\phi_2$

$$q^2 = \frac{K_1}{2}\left(1 + \frac{1}{\cos 2\phi_2}\right) + \frac{K_2}{2}\left(1 - \frac{1}{\cos 2\phi_2}\right)$$

Using (iv), (i) and (iii)

$$q^2 = \frac{K_1\rho_1 + K_2\rho_2}{2G} = \frac{K_1\rho_1 + K_2\rho_2}{\rho_1 + \rho_2}$$

Now putting

$$\left.\begin{aligned} K_1 &= 1 - A_1 \quad \text{where} \quad A_1 = \frac{r}{c'}\,[(\beta'^2 - r\beta') - \omega_x^2] \\ \text{and} \quad & \\ K_2 &= 1 - A_2 \quad \text{where} \quad A_2 = \frac{r}{c'}\,(\beta'^2 - r\beta'] \end{aligned}\right] \quad \dots \quad \text{(v)}$$

We get

$$q^2 = 1 - \frac{A_1\rho_1 + A_2\rho_2}{\rho_1 + \rho_2} \qquad \ldots \text{(vi)}$$

We have also :

$$L = \frac{r}{C''}(r - \beta')\omega_z \qquad \ldots \text{(vii)}$$

$$C'' = (\beta' - r)(\beta' + \rho_1\omega_z)(\beta' + \rho_2\omega_z) \qquad \ldots \text{(viii)}$$

Using (v) and (vii)

$$\rho_1 + \rho_2 = 2G = \frac{K_1 - K_2}{2L} = \frac{r\omega_x^2}{LC''} = \frac{\omega_x^2}{\omega_z(r - \beta')} \qquad \ldots \text{(ix)}$$

Using (ix), (v), (i), (ii)

$$\frac{A_1\rho_1 + A_2\rho_2}{\rho_1 + \rho_2} = -\frac{L}{\omega_z}(\beta' + \rho_1\omega_z) \qquad \ldots \text{(x)}$$

Using (x), (vii), (viii)

$$\frac{A_1\rho_1 + A_2\rho_2}{\rho_1 + \rho_2} = \frac{r}{\beta' + \rho_2\omega_z}$$

Hence

$$q^2 = K_1\cos^2\phi_2 + K_2\sin^2\phi_2 - 2L\sin\phi_2\cos\phi_2$$

$$= 1 - \frac{r}{\beta' + \rho_2\omega_z} = \text{square of the complex Refractive Index}$$

for the O-mode.

This is the same as Eqn. (5.1).

Similarly Eqs. (4.1), (4.2) and (5.2) can be deduced.

From Eqs. (i) and (iii), we get ... (xi)

$$\phi_2 - \phi_1 = \pi/2$$

Hence using (xi), (3.1) and (2.2)

$$W_1 = V_2$$

and using (xi), (3,2) and (2.1)

$$W_2 = -V_1$$

Using (12) and (12.1)

$$\dot{\phi}_1 = \dot{\phi}_2$$

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